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Electric-field-induced g/u mixing of the $E0_g^+(^3P_2)$ and $D0_u^+(^3P_2)$ ion-pair states of jet-cooled I_2 observed using optical triple resonance

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Electric-field-induced electronic state g/u mixing of nearly isoenergetic rovibrational levels of the $E0_g^+(^3P_2)$ and $D0_u^+(^3P_2)$ ion-pair states of I_2 has been observed using optical triple resonance combined with resonance ionization. Detectable mixing with applied fields of 1 kV/cm occurs over a range of energy level separations of $\leqslant 0.3\ cm^{-1}$. © *2004 American Institute of Physics.*
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I. INTRODUCTION

In a recent paper[1] we reported the observation of long-lived electronic states just below the first ion-pair dissociation threshold of I_2 by optical triple resonance, together with resonance ionization (OTR/RI), via the $B0_u^+$ valence and $E0_g^+(^3P_2)$ ion-pair states. During the course of subsequent experiments aimed at identifying the Rydberg states to which these long-lived states are coupled,[2] it was observed that some strong OTR/RI signals were observed when exciting via ($\nu=31$) of the $E0_g^+(^3P_2)$ ion-pair state that were not observed when exciting via any of the other levels in the range ($\nu=20-41$). These are identified as $f'0_g^+(^1D) \leftarrow D0_u^+(^3P_2)$ transitions. It will be shown that ($\nu=31$) of the $E0_g^+(^3P_2)$ ion-pair state can be coupled to ($\nu=37$) of the $D0_u^+(^3P_2)$ ion-pair state, with which it is almost isoenergetic, by the ~1 kV/cm extraction field in the time-of-flight mass spectrometer (TOFMS).

Two other examples of g/u transfer in I_2 have been observed experimentally. First, nuclear spin hyperfine coupling has been shown to induce g/u mixing of the $B0_u^+$ and $c1_g$ valence states. This mixing, first reported by Pique *et al.*[3] and reviewed by Bunker and Jensen,[4] has been used by several groups as a way of changing the g/u symmetry at the intermediate stage of double resonance excitation of ion-pair states.[5–8] Second, collisionally-induced g/u transfer, $D0_u^+(^3P_2) \leftarrow E0_g^+(^3P_2)$, has been investigated by several groups.[9–13] Akopyan *et al.*[10] studied the collision-induced rate constant as a function of the laser-excited rovibronic levels of the $E0_g^+(^3P_2)$ state. The cross sections are giant and there is a correlation between them and the energy gaps between the laser-excited and collisionally populated levels, the ($\Delta J=\pm 1$) transitions between nearly isoenergetic levels being most probable. Similar collision-induced g/u electronic energy transfer has also been observed in N_2 and N_2^+ by Katayama *et al.*[14–17]

The only previous example of external field-induced g/u mixing that we are aware of is that between high n,l Rydberg states of centrosymmetric molecules. Essentially, this is a perturbation of the rotational motion of the Rydberg electron resulting in l-state mixing, and since the inversion character of an atomic Rydberg molecule is (-1^l), there is also g/u mixing. Ion-pair states of diatomics can also be abnormally polarizable compared with ordinary valence states, but the polarizability tensor is now extremely anisotropic with the large component along the bond. The induction of a dipole necessarily destroys the g/u character, and in Sec. IV we will show that the higher vibrational levels of an ion-pair state in any given tier become increasingly susceptible to such mixing with field strengths commonly used in OTR/RI spectroscopy.

II. EXPERIMENT

The two-laser, three-color excitation scheme used previously[1] has been made more flexible by the addition of a third dye laser, enabling all three resonant stages to be independently tuned. The excitation pathway is illustrated in Fig. 1. The first pump photon, ν_1 (~553 nm), excites the (22,0) band of the $B0_u^+ \leftarrow X0_g^+$ transition. The second pump photon, ν_2 (350–385 nm), then excites a vibronic band in the range (20,22) to (58,22) of the $E0_g^+(^3P_2) \leftarrow B0_u^+$ transition. Finally, a probe photon, ν_3 (530–760 nm), excites transitions from the $E0_g^+(^3P_2)$ ion-pair state to Rydberg, ion-pair, or coupled Rydberg/ion-pair states below the first molecular ionization energy. These final states are then ionized by absorption of at least one more photon.

The experimental arrangement used to record the OTR/RI spectra comprised a system with three tunable lasers, a pulsed molecular beam, a TOFMS, and signal collection electronics. Three independently tunable dye lasers (two Lambda Physik FL3002's and a Lambda Physik FL2002) were pumped by a XeCl excimer laser (a Lambda Physik EMG201MSC). The ν_2 and ν_3 photons were introduced collinearly into the ionization chamber via a 6 cm focal length lens. The lens was positioned such that the beams were focused ~1 cm away from the detection region of the TOFMS.

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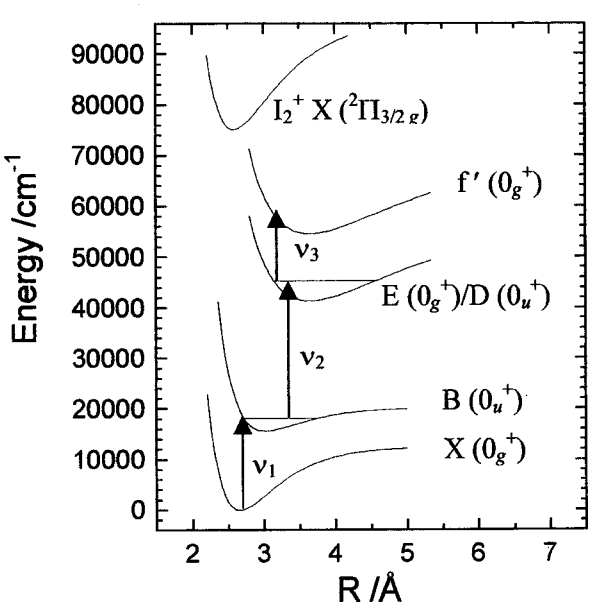

FIG. 1. The OTR/RI excitation pathway via a g/u mixed intermediate level. A single curve is used to illustrate both the $E0_g^+(^3P_2)$ and $D0_u^+(^3P_2)$ ion-pair states.

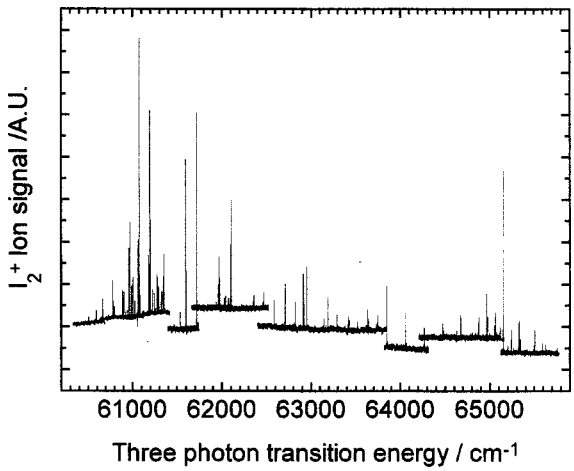

FIG. 2. An overview of the OTR/RI spectrum of I_2 over the three-photon transition energy range 60 300–65 800 cm^{-1}, recorded via ($\nu=41, J=25$) of the $E0_g^+(^3P_2)$ state. The spectrum is a composite of several scans and no attempt has been made to normalize the intensities.

The unfocused ν_1 photons were directed into the chamber at 180° to the other two beams.

The three-photon transition energies were determined by calculating the energies of the first two (pump) steps from the known molecular constants and adding the calibrated energy of the third (probe) step obtained in the present experiments. Probe laser wavelengths between 500 and 600 nm were calibrated from the I_2 fluorescence excitation spectrum and all others from neon optogalvanic lines, resulting in errors of ~0.2 and ~0.5 cm^{-1}, respectively. The term values were determined by adding the known rotational energy in the ground state to the three-photon transition energies.

The counterpropagating dye laser beams intersected the molecular beam at 90° between two electrodes separated by a distance of 1.6 cm. A high positive potential was applied to the upper electrode, while the lower electrode at the entrance to the TOF tube was grounded. The lower electrode contained a 1.5 mm diameter pinhole through which ions passed before entering the 52 cm long flight tube, which was terminated by a microchannel plate (MCP) detector.

The TOF spectra were recorded on a Lecroy 9344 digital oscilloscope by averaging the ion signal over 200 laser shots. The excitation spectra were recorded by processing the signal from the MCP detector with a Stanford Research SR250 boxcar and storing it on a PC.

Three ion-extraction modes were used. In the first, a dc extraction field of typically 1.25 kV/cm was applied. In the second, a pulsed extraction field of typically 950 V/cm and several microseconds duration was applied. This pulsed field was triggered by an electrical output from the excimer laser and timed so as to overlap the laser pulse. In the third mode, the same pulsed extraction field was applied but was triggered by the optical output of one of the dye lasers using a fast photodiode and timed so as to be delayed by at least 100 ns from the laser pulse.

The pulsed jet system was of conventional design and employed a commercial pulsed valve (General Valve, nozzle diameter 250 μm). Helium at a pressure of ~600 Torr was passed over solid I_2 at room temperature and the resulting mixture of I_2 and carrier gas expanded through the nozzle, which was warmed to ~310 K.

III. RESULTS

A. The excitation pathway

The most commonly used $B0_u^+ \leftarrow X0_g^+$ pump energy was 18 060.6 cm^{-1} (553.691 nm), corresponding to the $P(25)$ and $R(29)$ branches of the (22,0) band,[18] and hence ($J=24$ and 30) of the $B0_u^+$ state are excited. The most commonly used $E0_g^+(^3P_2) \leftarrow B0_u^+$ pump energy was 27 107.5 cm^{-1} (368.90 nm), corresponding to the $R(24)$ branch of the (41,22) band,[18,19] and hence ($J=25$) of the $E0_g^+(^3P_2)$ state uniquely is excited. A pump energy of 26 232.8 cm^{-1} (381.20 nm) was used to excite the same J level of ($\nu=31$) of the $E0_g^+(^3P_2)$ state. The probe photon wavelength was scanned between 770 and 530 nm (no dye was available to probe the range 670–695 nm).

B. OTR/RI spectra

An overview of the OTR/RI spectrum over the three-photon transition energy range 60 300–65 800 cm^{-1}, recorded via ($\nu=41, J=25$) of the $E0_g^+(^3P_2)$ state, is shown in Fig. 2. The spectrum is a composite of several scans and no attempt has been made to normalize the intensities.

The spectrum shown was recorded by monitoring the I_2^+ signal. All of the resonances were also observed, sometimes more strongly, by monitoring I^+. However, the I^+ channel also included at least two additional signals. First, it contained a two-color signal from the ν_1 and ν_2 photons, the intensity of which was constant for a particular vibrational level of the $E0_g^+(^3P_2)$ state but varied with ν. Second, when the wavelength of ν_3 was $\leqslant$630 nm, it could also excite $B0_u^+ \leftarrow X0_g^+$ transitions, which ν_2 could, at certain wave-

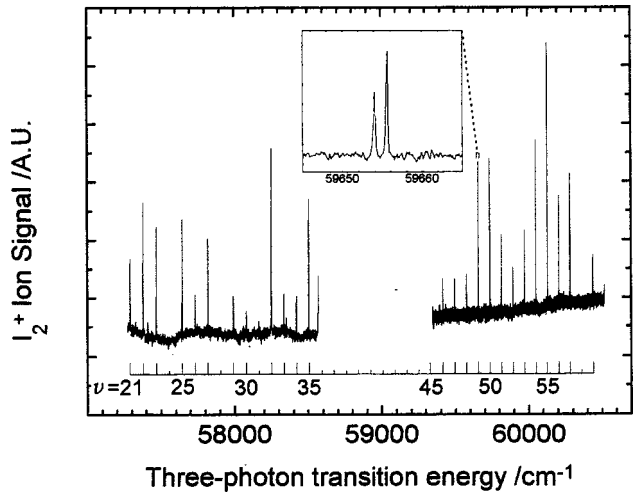

FIG. 3. The OTR/REMPI spectrum of I_2 over the three-photon transition energy range 57 300–60 500 cm^{-1}, recorded via ($\nu=31,J=25$) of the $E0_g^+(^3P_2)$ state. The numbering of the $f'0_g^+(^1D)$ ion-pair state vibrational progression is indicated. These bands are all *P, R* doublets, as illustrated by the inset, indicative of one-photon, parallel transitions.

lengths, further excite to the $E0_g^+(^3P_2)$ state and subsequently ionize. Since, in general, these two unwanted signals were not seen in the I_2^+ channel, this was used to obtain the OTR/RI spectra.

Throughout the spectrum shown in Fig. 2, only *P,R* doublets, indicative of parallel, one-photon transitions, were seen. The spectrum consists of *ungerade* Rydberg state vibrational levels that are homogeneously coupled to high vibrational levels ($\nu\sim400$) of the $D0_u^+(^3P_2)$ ion-pair state. The coupling of the Rydberg state(s) is indicated by irregular vibrational spacings, weak satellite structure around some vibrational levels, and irregular rotational splittings. These data will be described in more detail in a subsequent paper.[2]

When the three-photon region below 60 500 cm^{-1} was excited via ($\nu=31$) of the $E0_g^+(^3P_2)$ ion-pair state, a strong vibrational progression was observed, as shown in Fig. 3. This progression was not observed in spectra recorded via any other ($\nu,J=25$) level of the $E0_g^+(^3P_2)$ ion-pair state which was used, where ($\nu=20$, 24, 28, 30, 32, 35, and 41). The bands are all *P,R* doublets, as illustrated by the inset in Fig. 3, indicative of one-photon, parallel transitions. The average vibrational spacing of 85 cm^{-1} suggests that the progression is that of a third tier ion-pair state, i.e., dissociating to $I^+(^1D)+I^-(^1S)$.

The progression is almost certainly that of the $f'0_g^+(^1D)$ ion-pair state, as can be seen from the observed term values which are presented in Table I. The term value of the lowest-energy rotational level observed, relative to $X(\nu=0,J=0)$, is 57 313.1 cm^{-1}. This value agrees, to within our experimental accuracy ($\sim\pm0.5$ cm^{-1}), with the term value of 57 313.4 cm^{-1} calculated for ($\nu=21,J=23$) of the $f'0_g^+(^1D)$ state using molecular constants[20] that are valid up to ($\nu=20,J=117$). Furthermore, the observed vibrational spacings over the range ($\nu=22-59$) are also consistent with those generated by the vibrational constants, valid up to ($\nu=166$) reported by Wilson *et al.*[21] Thus, it is concluded that transitions to the $f'0_g^+(^1D)$ state are being observed and the bands in Fig. 3 and their term values in Table I are labeled accordingly.

TABLE I. Observed term values ($\sim\pm0.5$ cm^{-1}) of ($J=23$), relative to $X(\nu=0,J=0)$, of several vibrational levels of the $f'0_g^+(^1D)$ ion-pair state of I_2, together with the observed and literature (Ref. 21) vibrational spacings.

ν	Observed term value (cm^{-1})	Observed $\nu-(\nu-1)$ (cm^{-1})	Literature $\nu-(\nu-1)$ (cm^{-1})
21	57 313.1	⋯	⋯
22	57 402.6	89.5	89.0
23	57 490.8	88.2	88.7
24	⋯	⋯	88.3
25	57 667.5	⋯	88.0
26	57 754.9	87.4	87.6
27	57 841.6	86.7	87.3
28	⋯	⋯	86.9
29	58 015.1	⋯	86.6
30	58 101.3	86.2	86.2
31	58 187.7	86.4	85.9
32	58 273.3	85.6	85.6
33	58 358.1	84.8	85.2
34	58 442.7	84.6	84.9
35	58 527.3	84.6	84.5
-	⋯	⋯	⋯
45	59 354.1	⋯	⋯
46	59 435.3	81.2	80.9
47	59 516.1	80.8	80.6
48	59 596.2	80.1	80.3
49	59 676.1	79.9	80.0
50	59 755.8	79.7	79.7
51	59 834.9	79.1	79.3
52	59 913.7	78.8	79.0
53	59 992.9	79.2	78.7
54	60 071.2	78.3	78.4
55	60 149.1	77.9	78.1
56	60 227.1	78.0	77.8
57	60 304.1	77.0	77.5
58	⋯	⋯	77.2
59	60 457.6	⋯	76.8

The assignment of the progression shown in Fig. 3 as that of the $f'0_g^+(^1D)$ state implies that the probe step is a $g\leftarrow g$ transition. However, this observation can be explained by invoking a coupling of ($\nu=31,J=25$) of the $E0_g^+(^3P_2)$ ion-pair state with ($\nu=37,J=24$) of the $D0_u^+(^3P_2)$ ion-pair state. The interpretation is supported by a consideration of the term values of the rovibronic levels of the $E0_g^+(^3P_2)$ and $D0_u^+(^3P_2)$ ion-pair states in this energy region. The term values of ($J=0-40$) of ($\nu=31$) of the $E0_g^+(^3P_2)$ state and ($\nu=37$) of the $D0_u^+(^3P_2)$ state, calculated from the published molecular constants,[19,22] are presented in Table II. The range of J levels shown is that which we were able to excite in the present molecular beam (cooled molecule) experiments. It can be seen that ($\nu=31,J=25$) of the $E0_g^+(^3P_2)$ ion-pair state is separated from ($\nu=37,J=24$) of the $D0_u^+(^3P_2)$ ion-pair state by only 0.17 cm^{-1}. In contrast, ($\nu=30,J=25$) and ($\nu=32,J=25$) of the $E0_g^+(^3P_2)$ ion-pair state are separated from ($\nu=36,J=24$) and ($\nu=38,J=26$) of the $D0_u^+(^3P_2)$ ion-pair state, the nearest levels with ($\Delta J=\pm1$), by 4.13 and 2.46 cm^{-1}, respectively. Coupling between these pairs of levels is not observed. It can be seen from Table II that the small energy separation between

TABLE II. Calculated term values, relative to $X(\nu=0,J=0)$, of some rovibronic levels of the $E0_g^+(^3P_2)$[19] and $D0_u^+(^3P_2)$ (Ref. 22) ion-pair states of I_2.

J	$E(\nu=31)$ (cm^{-1})	$D(\nu=37)$ (cm^{-1})	$E(\nu=53)$ (cm^{-1})	$D(\nu=60)$ (cm^{-1})
0	44 305.68	44 306.01	46 183.80	46 183.90
1	44 305.71	44 306.05	46 183.83	46 183.93
2	44 305.79	44 306.13	46 183.90	46 184.01
3	44 305.90	44 306.24	46 184.01	46 184.11
4	44 306.04	44 306.39	46 184.14	46 184.26
5	44 306.22	44 306.58	46 184.31	46 184.43
6	44 306.44	44 306.81	46 184.52	46 184.65
7	44 306.70	44 307.08	46 184.76	46 184.90
8	44 306.99	44 307.38	46 185.03	46 185.18
9	44 307.32	44 307.72	46 185.34	46 185.51
10	44 307.69	44 308.10	46 185.68	46 185.86
11	44 308.09	44 308.52	46 186.06	46 186.26
12	44 308.53	44 308.97	46 186.47	46 186.69
13	44 309.00	44 309.47	46 186.92	46 187.15
14	44 309.52	44 310.00	46 187.40	46 187.65
15	44 310.06	44 310.56	46 187.91	46 188.19
16	44 310.65	44 311.17	46 188.46	46 188.76
17	44 311.27	44 311.82	46 189.04	46 189.36
18	44 311.93	44 312.50	46 189.66	46 190.01
19	44 312.62	44 313.22	46 190.31	46 190.69
20	44 313.35	44 313.98	46 191.00	46 191.40
21	44 314.12	44 314.77	46 191.72	46 192.15
22	44 314.93	44 315.61	46 192.47	46 192.94
23	44 315.77	44 316.48	46 193.26	46 193.76
24	44 316.64	44 317.39	46 194.08	46 194.62
25	44 317.56	44 318.34	46 194.94	46 195.51
26	44 318.51	44 319.32	46 195.83	46 196.44
27	44 319.49	44 320.35	46 196.76	46 197.40
28	44 320.52	44 321.41	46 197.71	46 198.40
29	44 321.58	44 322.51	46 198.71	46 199.44
30	44 322.67	44 323.65	46 199.74	46 200.51
31	44 323.81	44 324.82	46 200.80	46 201.62
32	44 324.98	44 326.04	46 201.90	46 202.76
33	44 326.18	44 327.29	46 203.03	46 203.94
34	44 327.43	44 328.58	46 204.19	46 205.15
35	44 328.70	44 329.90	46 205.39	46 206.40
36	44 330.02	44 331.27	46 206.62	46 207.69
37	44 331.37	44 332.67	46 207.89	46 209.01
38	44 332.76	44 334.11	46 209.19	46 210.36
39	44 334.19	44 335.59	46 210.53	46 211.76
40	44 335.65	44 337.10	46 211.90	46 213.18

($\nu=31,J$) of the $E0_g^+(^3P_2)$ and ($\nu=37,J-1$) of the $D0_u^+(^3P_2)$ ion-pair states only varies slightly in the range ($J=10-40$). This, we suggest, is why it has been possible to observe transitions to the $f'0_g^+(^1D)$ ion-pair state throughout this range of rotational levels.

A calculation of the rotational term values of the vibrational levels of the $E0_g^+(^3P_2)$ and $D0_u^+(^3P_2)$ states using the known molecular constants[19,22] reveals that the only other pair of vibrational levels, for ($\nu\leqslant 70$) of the $E0_g^+(^3P_2)$ state, in which the separation of the rotationless levels is $\leqslant 0.5$ cm^{-1}, are ($\nu=53$) of the $E0_g^+(^3P_2)$ state and ($\nu=60$) of the $D0_u^+(^3P_2)$ state. The rotational term values of these two levels are also shown in Table II. Coupling between these vibrational levels has been confirmed by the observation of $f'0_g^+(^1D)\leftarrow D0_u^+(^3P_2)$ transitions using rotational levels up to ($J=30$), the highest J level that was tried.

The $F'0_u^+(^1D)$ ion-pair state, i.e., the third tier ion-pair state that is accessed by a parallel transition from the $E0_g^+(^3P_2)$ state, has been characterized up to $\sim 56\,100$ cm^{-1} ($\nu=38$) by Ishiwata *et al.*[23] It is not possible to say whether or not the term values in Table I are also consistent with those of the $F'0_u^+(^1D)$ state, as a calculation of the latter involves too large an extrapolation of the published constants. However, $F'0_u^+(^1D)\leftarrow E0_g^+(^3P_2)$ transitions should be strong and if, as it appears, they are not observed in the $57\,000-60\,500$ cm^{-1} three-photon energy region in spectra recorded via every vibrational level of the $E0_g^+(^3P_2)$ state, then their absence must be explained. The range of $f'0_g^+(^1D)$ state vibrational levels ($\nu=21-59$) observed via parallel transitions from ($\nu=37$) of the $D0_u^+(^3P_2)$ state is consistent with the Franck–Condon overlap between the two states. Since T_e of the $F'0_u^+(^1D)$ state lies ~ 4000 cm^{-1} below that of the $f'0_g^+(^1D)$ state, transitions to ($\nu=21-59$) of the $F'0_u^+(^1D)$ state from ($\nu=20-40$) of the $E0_g^+(^3P_2)$ state require probe photons that are out of the range that can be generated by our laser system. Hence, no such $F'0_u^+(^1D)\leftarrow E0_g^+(^3P_2)$ transitions are observed in the present experiments.

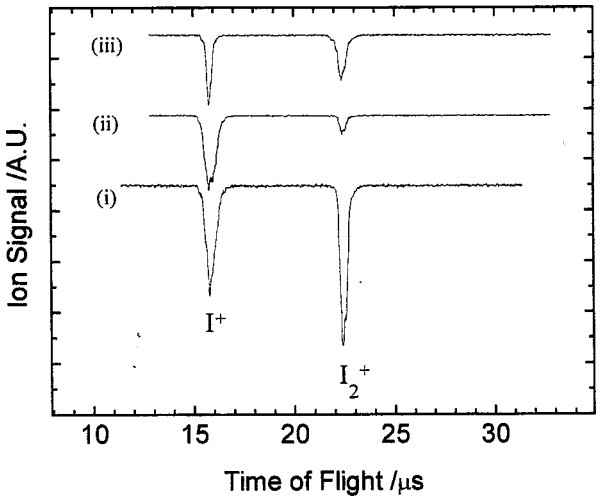

FIG. 4. TOF spectra observed by OTR/RI using a dc extraction field of 1.25 kV/cm and various excitation pathways: (i) ''Rydberg''$\leftarrow(\nu=41,J=25)$ $E0_g^+(^3P_2)$, (ii) ''ion-pair''$\leftarrow(\nu=41,J=25)$ $E0_g^+(^3P_2)$, and (iii) $f'0_g^+(^1D)\leftarrow(\nu=31,J=25)$ $E0_g^+(^3P_2)/(\nu=37,J=24)$ $D0_u^+(^3P_2)$.

C. TOF spectra

All of the OTR/REMPI spectra were obtained using a dc extraction field of ~ 1.25 kV/cm. Three typical TOF spectra recorded under these extraction conditions are shown in Fig. 4. Spectrum (i) was obtained by exciting out of ($\nu=41,J=25$) of the $E0_g^+(^3P_2)$ state into a coupled Rydberg/ion-pair level that is predominantly Rydberg in character. Spectrum (ii) was obtained by exciting out of the same rovibronic level into a similarly coupled state but one that has predominantly ion-pair character. Spectrum (iii) was obtained by exciting out of ($\nu=31,J=25$) of the $E0_g^+(^3P_2)$ state into the $f'0_g^+(^1D)$ state as a result of its coupling to ($\nu=37,J=24$) of the $D0_u^+(^3P_2)$ state.

In a preparatory experiment for a delayed pulsed-field extraction, an 8 μs, 950 V/cm extraction pulse that overlaps

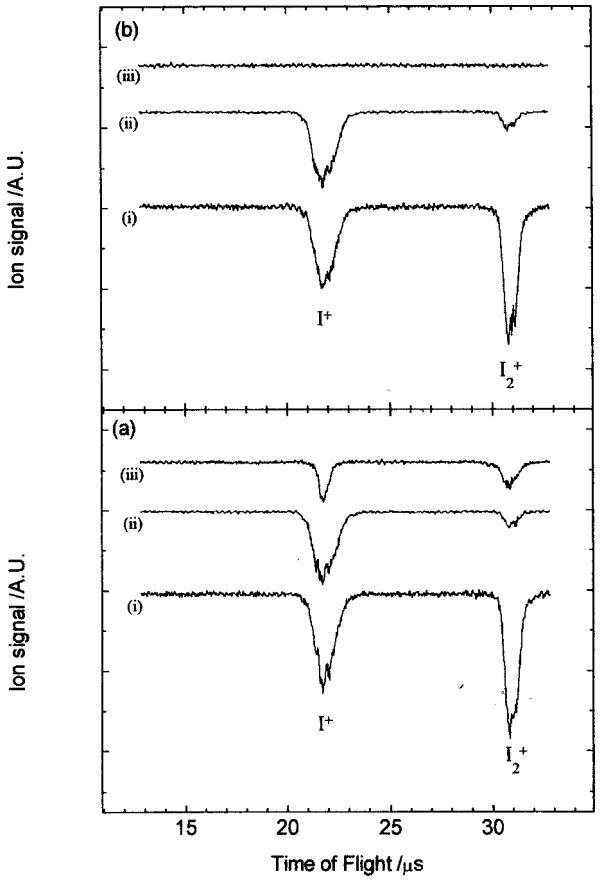

FIG. 5. TOF spectra observed by OTR/RI using the same excitation pathways as in Fig. 4 and pulsed extraction fields of 950 V/cm, 8 μs in length; (a) overlapping the laser pulse in time and (b) delayed from the laser pulse by ~150 ns. The flight times are different from those in Fig. 4 as a result of the difference in the magnitudes of the extraction pulse.

the laser pulse in time is applied. Figure 5(a) shows the resultant TOF spectra, obtained via the same three excitation pathways as were used to record the TOF spectra shown in Fig. 4. The relative intensities of the three spectra are essentially the same as those obtained using a dc field. The flight times are longer as a result of the difference in the magnitude of the field.

However, when the same three excitation pathways are used, but with an 8 μs, 950 V/cm extraction pulse delayed by ~150 ns after the laser pulse, there is no signal observed via the $E0_g^+(^3P_2)$ $(\nu=31,J=25)/D0_u^+(^3P_2)$ $(\nu=37,J=24)$ coupled levels, although large signals are still seen via the other two pathways (i) and (ii), as can be seen in Fig. 5(b)(iii). Thus, it can be concluded that the coupling of the $(\nu=31,J=25)$ $E0_g^+(^3P_2)$ and $(\nu=37,J=24)$ $D0_u^+(^3P_2)$ levels is only observed in the presence of an electric field. Similar TOF profiles have been used to confirm the field-induced coupling between $(\nu=53,J)$ of the $E0_g^+(^3P_2)$ state and $(\nu=60,J-1)$ of the $D0_u^+(^3P_2)$ state for all values of J in the range $(J=0-30)$ that were tried.

IV. DISCUSSION

If the parallel electronic transition dipole between two electronic states $|1\rangle$ and $|2\rangle$ is $\mu_{12}(R)$ and the first-order mixed wave functions are written

$$|1'\rangle=|1:\nu_1,J_1M_1\rangle+c(R)|2:\nu_2,J_2M_2\rangle, \quad (1)$$

$$|2'\rangle=-c(R)|1:\nu_1,J_1M_1\rangle+|2:\nu_2,J_2M_2\rangle, \quad (2)$$

then the coefficient of mixing with the external field, F, along the laboratory z axis is

$$c(F,R)=\frac{\langle\nu_1|\mu_{12}(R)|\nu_2\rangle\langle J_1M_1|\cos\theta|J_2M_2\rangle}{E_2(\nu_2,J_2)-E_1(\nu_1,J_1)}F. \quad (3)$$

The energy levels themselves are Stark-shifted by $\pm c^2[E_2(\nu_2,J_2)-E_1(\nu_1,J_1)]$. It is clear from the Hönl–London factor in Eq. (3) that, for a molecule in an $\Omega=0$ state, only rotational states differing by $\Delta J=\pm1$ can be mixed.

Ion-pair states are particularly susceptible to field-induced g/u mixing, as can be illustrated by the mixing of the $E0_g^+(^3P_2)$ and $D0_u^+(^3P_2)$ state states of I_2. These two states dissociate to give the same pair of ion states, $I^+(^3P_2)$ and $I^-(^1S)$. Consequently,[24] there is a giant transition dipole between them which behaves as

$$\langle D|\mu_z|E\rangle\rightarrow eR_{AB}, \quad (4)$$

as $R\rightarrow\infty$. This result follows immediately from the pure precession description of ion-pair states which is good at large R (see Ref. 24 and references therein for further details). Since this must always be a parallel transition, the selection rule for field-induced coupling is $\Delta\Omega=0$. If two bound electronic states converge on the same limit, nearly isoenergetic vibrational levels in each of the two states will increasingly tend to have the same outer turning point, $R_>$. The corresponding vibrational wave functions will then have significant overlap near their outer turning points. Combined with the linearly increasing transition dipole, the vibrational matrix element in (3) can then be approximated by $\mu(R_>)\langle\nu_E\nu_D\rangle$. $R_>$ for one pair of vibrational levels involved in the coupling, ($\nu_E=31$), ($\nu_D=37$) is 4.4 Å and the difference in turning points is ~0.02 Å.[19,25] When the two potentials are approximated by Morse functions that have the observed D_e values and give the two observed ω_e values, the resulting overlap $\langle 31|37\rangle$ equals 0.16. If this value, together with a Hönl–London factor of $1/\sqrt{6}$, appropriate to $J\gg1$, and $F=1$ kV/cm is inserted into Eq. (3), then, for c to be greater than, say, 0.1, an energy separation of less than 0.23 cm^{-1} is required. In practice, these Franck–Condon factors and the associated matrix elements $\langle\nu_E|R|\nu_D\rangle$ are very sensitive to the difference in the outer turning points of the two vibrational states, as has been found by Akopyan *et al.*[10] In the actual experiment, the $E0_g^+(^3P_2)$ state is accessed by two photons polarized in the z direction. Consequently, the M_J-state population is biased in favor of low M_J states (i.e., there is partial alignment) and hence the Hönl–London factor tends to the limit of 1/2 for a purely $M_J=0$ population. This does not alter the conclusion that a field strength of ~1 kV/cm is sufficient to appreciably mix vibrational levels of the $E0_g^+(^3P_2)$ and $D0_u^+(^3P_2)$ states when their energy separation is $\leqslant$0.3 cm^{-1}.

In the present experiments, field-induced coupling, with a field of 1.25 kV/cm, has been detectable between rovibronic levels that are separated, according to the published molecular constants,[19,22] by up to 0.3 cm^{-1}. This experimen-

tal upper limit to the separation is defined by a combination of the population of ground-state rotational levels in the molecular beam (high-J limit) and the extent to which a rotational level in the $E0_g^+(^3P_2)$ state can be uniquely excited (low-J limit). A different pair of vibronic levels or a room-temperature experiment will have to be used to determine a true upper limit to the separation over which coupling can be detected using this particular magnitude of field.

The separations that are given here are derived from term values calculated from molecular constants reported in the literature and will have errors of the order of tenths of wave numbers. In order to determine experimentally a true upper level to the separation over which coupling can be detected, it will be necessary to discriminate between the individual components of a coupled pair of rotational levels. If the separations of the coupled levels are truly $\leqslant 0.3\ cm^{-1}$, it is not surprising that we have been unable to do this as the bandwidth of our lasers is $\sim 0.2\ cm^{-1}$.

Mixing of several other pairs of vibronic levels in I_2 can be predicted using known vibrational constants.[7,26–28] For example, if it is assumed that a pair of vibronic bands whose rotationless levels are separated by $\sim 1\ cm^{-1}$ may have higher rotational levels that are separated by $\leqslant 0.3\ cm^{-1}$, then coupling may occur between ($\nu = 18$) of the $\beta 1_g(^3P_2)$ state and ($\nu = 11$) of the $\gamma 1_u(^3P_2)$ state and ($\nu = 10$) of the $G1_g(^3P_1)$ state and ($\nu = 3$) of the $H1_u(^3P_1)$ state. In addition, while I_2 is a particularly favorable example because it has a high density of states, there is no reason why the same mixing should not also be observable in the ion-pair states of the lighter halogens and the alkali metal dimers, whose ion-pair states have been widely studied.

$D0_u^+(^3P_2) \leftarrow E0_g^+(^3P_2)$ collisional transfer is also favored by the large transition dipole between the states. If, in addition, the energy gaps between the laser-excited and collisionally populated levels ($\Delta J = \pm 1$), are small, then giant cross sections are observed. This is particularly true for transfer from ($\nu = 32, J = 55$) of the $E0_g^+(^3P_2)$ state to ($\nu = 38$, $J = 54$ and 56) of the $D0_u^+(^3P_2)$ state, where the energy gap was reported[10] to be only $\sim 2\ cm^{-1}$. Indeed, by using revised[22] molecular constants for the $D0_u^+(^3P_2)$ state, the ($\Delta J = +1$) gap is reduced to less than $0.7\ cm^{-1}$. This gap represents the nearest coincidence that was achievable in the experiments of Akopyan *et al.*,[10] where only ($\nu, J = 55$) in the $E0_g^+(^3P_2)$ state could be excited. It is possible that the rate constants for collisional transfer between the levels discussed in the present paper, where the energy gap is $\sim 0.2\ cm^{-1}$, may be even larger.

V. CONCLUSIONS

Electric-field-induced electronic state g/u mixing of nearly isoenergetic rovibrational levels ($\Delta J = \pm 1$) of the $E0_g^+(^3P_2)$ and $D0_u^+(^3P_2)$ ion-pair states of I_2 has been observed. Detectable mixing occurs over a range of energy level separations of $\leqslant 0.3\ cm^{-1}$ with applied fields of 1 kV/cm. It has been shown that pairs of ion-pair states with a common Ω and dissociation products are particularly favorable for this form of mixing as a consequence of the giant transition dipole between them and their very similar outer turning points. Using these criteria, mixing of several other pairs of vibronic levels in I_2 can be predicted.

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